PHOTOELECTRON-PHOTOION COINCIDENCE STUDY OF BENZONITRILE

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ABSTRACT

The technique of photoelectron-photoion coincidence with variable ion source residence times has been applied to a study of benzonitrile ion fragmentation. The breakdown curve of the parent ions shows a strong dependence on residence time. Detailed analysis of this dependence shows that the ion fragments from its electronic ground state via a "tight" activated complex, in agreement with the conclusions of Chesnavich and Bowers. The rate-energy dependence agrees with that determined by Eland and Schulte, and the fragmentation threshold is in reasonable agreement with the threshold observed in electron impact at very long ion source residence times. The results lead to $\Delta H^{\circ}_{f_0}(C_6H_4^+) = 1321 \pm 10$ kJ/mol. The energetics of additional neutral and ionic C_6H_4 isomers is estimated and discussed.

RESUME

La technique de coïncidence photoélectron-photoion, avec des temps de résidence variables dans la source d'ions, a été appliquée à l'étude de la fragmentation de l'ion benzonitrile. La courbe de fragmentation de l'ion parent dépend fortement du temps de résidence. Une analyse détaillée de cette dépendance montre que l'ion se fragmente à partir de l'état électronique fondamental par l'intermédiaire d'un complexe activé "rigide" en accord avec les conclusions de Chesnavich et Bowers.

La dépendance vitesse-énergie est en accord avec celle déterminée par Eland et Schulte et le seuil de fragmentation concorde raisonnablement avec le seuil observé par bombardement électronique pour des temps de résidence dans la source de l'ion très longs. Les résultats conduisent à $\Delta H^{\circ}_{f_0}(C_6H_4^+) = 1321 \pm 10$ KJ/mol. Les données énergétiques pour d'autres isomères neutres ou ioniques de C_6H_4 sont estimées et discutées.

Introduction

Two basic items of information about an ion fragmentation process are its energy threshold and the dependence of the fragmentation rate on the excitation energy in excess of the threshold value. For large molecule ions, the determination of an energy threshold is made difficult by a number of factors including the slow fragmentation rate, the significant thermal energy content of the sample molecule itself as well as the difficulty in defining the energy distribution of the ion produced by photon or electron impact. As for the energy dependence of the rate constant, its determination requires an accurate knowledge of the effective parent ion residence time in the apparatus as well as a careful analysis of the effects of the excitation energy distribution on observable fragmentation behavior. The observable behavior is always the result of the fragmentation of a group of ions with a distribution of rates. There is no reason to suppose that this distribution is uniform in some narrow interval, nor that simple average quantities can be determined.

The effect of slow decomposition kinetics on measurements of fragmentation thresholds, the so-called kinetic shift, were pointed out many years ago (1,2) Gross (3), Lifshitz et al. (4) and Gordon and Reid (5) have demonstrated directly the effect of varying ion residence time on electron impact appearance potentials of large fragment ions. Vestal (6) and Potzinger and von Bünau (7) performed QET calculations to estimate the magnitude of the displacement of the observable onset from the true threshold value. Other workers have studied this kinetic effect by comparing the appearance potential of the fragmentation formed in the mass spectrometer ion source with that of the delayed fragmentation observed as a metastable transition, often with conflicting results (8-13).

A completely different approach is based on the study of the decay behavior of ions of more or less known excitation energy. These can be produced by photoionization with helium 58.4 nm radiation combined with selection of a narrow energy band of photoelectrons (14-16). Alternatively, variable photon wavelength can be combined with selection of electrons of essentially zero energy (17-21). Ions of more or less defined internal energy have also been produced and studied by means of charge exchange (22) and implicitly by means of second derivative electron impact techniques (23). In all cases, the ions have a spread in internal energy because of the finite resolution of the photoelectron energy selector, energy transfer in charge exchange, or energy spread of the ionizing electron or photon

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beam. More fundamentally, the sample molecules have a non-negligible internal thermal energy as well as external rotational energy. It is entirely possible that this rotational energy may be available for fragmentation.

The purpose of the present study is to determine the energy threshold and energy dependent fragmentation rate for the process

$$C_6H_5CN^+ \rightarrow C_6H_4^+ + HCN$$

using the recently developed technique of photoelectron-photoion coincidence with variable ion residence time (24-26). This process was chosen for study because it is somewhat more complex thant the three processes studied previously by this technique. It has a high activation energy and, consequently, should have a large kinetic shift of the measured threshold. It has been the subject of numerous electron impact studies aimed at determining the magnitude of this kinetic shift. The varied results have been summarized and discussed by Gordon and Reid (5). Also, there have been two determinations of the energy dependence of the fragmentation rate, one by means of charge exchange (22), the other by electron ion coincidence using helium resonance radiation and electron energy selection (27). The coincidence experiment yielded a rate-energy dependence parallel to that from the charge exchange experiment but displaced about 0.4 eV higher on the energy axis. The difference was attributed to collisional energy transfer in the charge exchange experiment.

The energy dependence of this rate, as determined by Andlauer and Ottinger (22) was studied theoretically by Klots (28), using his formulation of unimolecular rate theory (29). The results were unsatisfactory. More recently, Chesnavich and Bowers (30) were able to account for the energy dependence of the rate, as determined by Eland and Schulte (27), using standard QET-RRKM formalism. The central difference between the Klots study and the Chesnavich-Bowers study is that the Klots rate formalism is essentially a final state formalism which can be regarded as equivalent to a transition state formalism with a very loose transition state. The QET-RRKM formalism allows for tight as well as loose transition states, although it is deficient in some details of angular momentum conservation. Chesnavich and Bowers found in fact that the experimental rate-energy dependence could be accounted for by a rather tight transition state. In both studies the energy threshold was taken as a fixed quantity, 4.65 eV in the Klotz study and 3.09 eV in the later study. In the present work both the energy threshold and the transition state characteristics will be determined. Also, the rate-energy dependence will be established and compared with the two earlier determinations.

Experimental

The experimental data were obtained with the threshold photoelectron-photoion coincidence spectrometer described previously (31). The sample gas is ionized by a monochromatized photon beam. The resulting photoelectrons are drawn out by a very weak field and filtered through a steradiancy analyzer and cylindrical sector analyzer so that only electrons with near-zero initial energy are detected. Following detection of such an electron, a drawout pulse is applied to the ion source region and the positive ion is accelerated through an accelerating-focussing lens system and a drift region. It is detected by a multiplier, in delayed coincidence with the electron pulse. The mass is determined by the time-of-flight, using standard electronic techniques. The electron filtering arrangement assures that the excitation energy of the ion is accurately known, if the ionization potential of the molecule is accurately known. The actual narrow distribution of ion internal energies sampled in this system is established by studying the electron collection efficiency above the krypton $^2P_{1/2}$ ionization threshold (31). The half width of this distribution is 28 meV. It is not symmetrical, having a pronounced low energy tail resulting from some acceptance of higher energy electrons which are initially directed towards the electron filter.

The nominal parent ion residence time in the source region is determined by the electron transit time and the turn-on and rise time of the pulsing system. It is at the minimum 0.70 μs. It can be increased by deliberately delaying the application of the drawout pulse. The maximum tolerable delay is dictated by ion losses due to drifting in the ion source region. In the present study the nominal delays employed were 0.70 and 3.80 μs. The actual effective residence time is somewhat longer, as is discussed later. The time of flight spectra are similar in appearance to those for chlorobenzene (25) and bromobenzene (26). Between the TOF peaks corresponding to parent and fragment there is a distribution of counts at intermediate travel times. These come from dissociations occurring in the acceleration-focussing lens region, i.e. metastable transitions. With the application of the drawout pulse, ion fragmenting shortly thereafter will have a travel time only a little longer than a fragment formed just prior to application of the drawout pulse. Thus it is necessary to define a time of flight range in which the ions are defined as fragments and to calculate the additional time after pulse application which produces fragments lying within this time range. Under the conditions and definitions of the present experiment this amounted to 0.37 μs, which has to be added to the drawout pulse delays. The rest of the ions, metastables included, are then defined as parents, i.e. ions which have not decomposed within that time. Another time can be defined by counting all metastable transitions as fragments. The corresponding time is then the pulse delay time plus the parent ion travel time through the acceleration region. In this manner it was possible to obtain data for as a third effective residence time from the second definition, 6.9 μs. With this procedure it is possible to take into account all observable fragmentation and non-fragmentation events in a self consistent manner and determine a breakdown curve at different ion source residence times, see Figure 1.

Analysis of the data

The breakdown curves were analyzed in the same manner as previously (24-26), except for the treatment of external rotations (see below). The reactant ion frequencies were taken to be the same as those of neutral benzonitrile, and the set of rounded values tabulated by Chesnavich and Bowers was used (30). This corresponds quite well to the actual frequencies of the molecule (32). A symmetry factor of 2 was used for the activated complex and, following Chesnavich and Bowers, a normal mode of 800 cm^{-1} was taken as the reaction coordinate, and two normal modes of initial value 3100 and 450 cm^{-1} were taken as adjustable parameters.

Properly averaged breakdown curves were calculated for the three effective residence times taking into account the apparatus sampling function and the thermal distribution of vibrational populations by means of numerical convolutions. In contrast to the earlier studies, calculations were carried out on two sets of as-

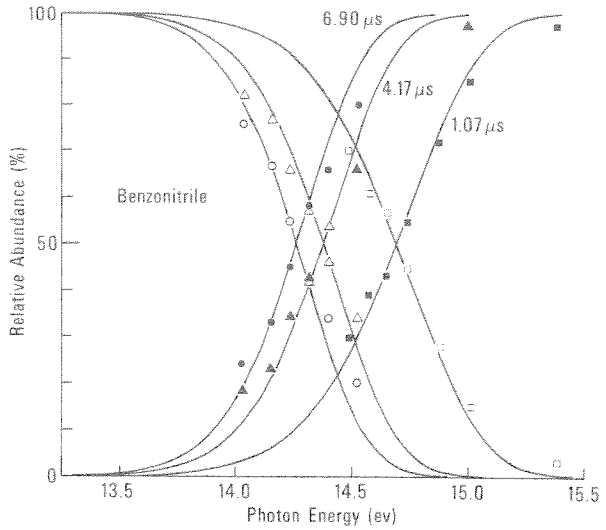

Fig. 1. — Breakdown curves for benzonitrile for 1.07, 4.17 and 6.90 μs effective residence times. Experimental points: (○), (△), (□) $C_6H_5CN^+$ parent; (●), (▲), (■) $C_6H_4^+$ fragment; (—) best fit calculations. The thermochemical threshold lies at 12.72 ± 0.03 eV.

sumptions, namely that the external rotational energy distribution was available or not available for fragmentation. From the averaged breakdown curves the photon energy at which 50 % fragmentation takes place was calculated for the 1.07 and 4.17 μs effective residence times, thus defining the long time (4.17 μs) crossover energy and the shift in this crossover energy at the short residence time (1.07 μs). From several sets of such calculations a family of curves was constructed showing the dependence of the crossover energy and crossover shift on the value of the activation energy and the equivalent activation entropy, defined as the activation entropy at 1000°K calculated for the hypothetical thermal unimolecular reaction with the same activated complex parameters. The results are shown in Figure 2 along with two points corresponding to the experimental crossover energy, 14.37 ± 0.015 eV and crossover shift, 0.32 ± 0.02 eV determined in this work and the values

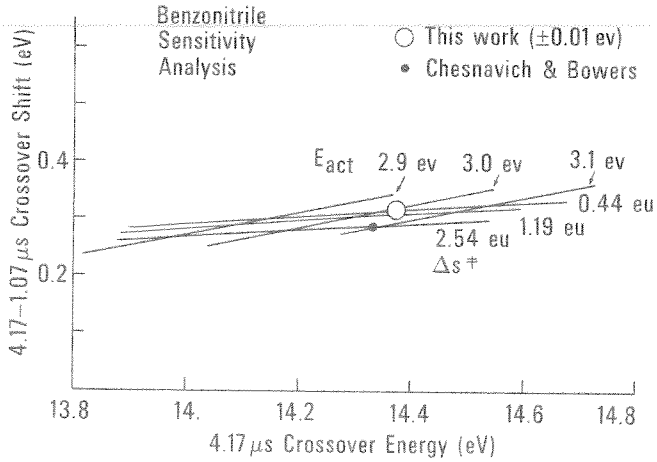

Fig. 2. — Sensitivity of the calculated benzonitrile breakdown curves to activation energy, E_{act}, and activation entropy. The curves show the change in the crossover energy (energy at the 50 % point in the long time parent-fragment curves) and the change in the crossover shift (energy difference between the crossover points of the breakdown curves obtained at two different times). (○) Crossover energy and shift obtained from Figure 1. (●) Crossover energy and shift calculated using parameters from reference 30.

deduced by calculations with the activated complex model given by Chesnavich and Bowers. It is seen that the two quantities are somewhat different, leading to different predictions of breakdown behavior.

Results and discussion

The above sensitivity analysis led to a best set of activated complex parameters and an activation energy which were used to calculate averaged breakdown curves for all three effective residence times. These curves are shown in Figure 1. It is seen that the time behavior of the experimental breakdown is reproduced rather well. There is some indication of slightly slower variation, which may represent some slight uncertainty in the actual form of the apparatus sampling function and uncertainty in the correction for accidental coincidences. The parameters are given in Table I for both contribution of rotational energy to fragmentation and no rotational contribution. The actual curves shown represent calculations with no rotational contribution. The other model fits the breakdown data equally well, but with slightly different parameters. Also given in Table I are the data used by Chesnavich and Bowers. Auxiliary thermochemical data are given in Table II. As mentioned above, the kinetic parameters used by Chesnavich and Bowers lead to a different breakdown behavior. This is clearly shown in Figure 3 where breakdown curves are shown both for our best fit parameters as well as theirs. Inspection of Table 1 shows that, although the absolute differences are quite small, the effect on breakdown curves is very pronounced. This is one more illustration of the sensitivity of this method of analysis which was noted at the outset (24).

TABLE I

Kinetic parameters for Benzonitrile Ion Fragmentation

E_{act}, eV	$\Delta S^{\neq}_{1000}$, cal/deg	A_{1000} sec^{-1}	External Rotations	Ref.
3.015	0.4	1.6×10^{13}	Inactive	This work
3.035	0.4	1.6×10^{13}	Active	This work
3.092	2.5	4.5×10^{13}	Inactive	30
3.077	---	---	---	a

a. Calculated from ΔH_f° ($C_6H_4^+$) determined in reference 43 and auxiliary thermochemical values.

TABLE II

Auxiliary Thermochemical Data

Species	$\Delta H_{f_{298}}^\circ$, kJ/mol	$\Delta H_{f_0}^\circ$ kJ/mol	Ref.
C_6H_5CN	215.7 ± 2.1	230 ± 2.1	51,a
$C_6H_5CN^+$	--	1166 ± 3	b
HCN	--	136 ± 8	55

a. The 0K value was computed using the vibrational frequencies determined by Jakobsen.[32]

b. Computed using an average ionization potential of 9.70 eV.[52-54]

We agree with the principal qualitative conclusion of Chesnavich and Bowers, namely, that this fragmentation process proceeds via a tight complex rather than a loose ion-dipole complex. Hence the formulation of Klots is not applicable. As for the activated complex parameters themselves, Chesnavich and Bowers only lowered one

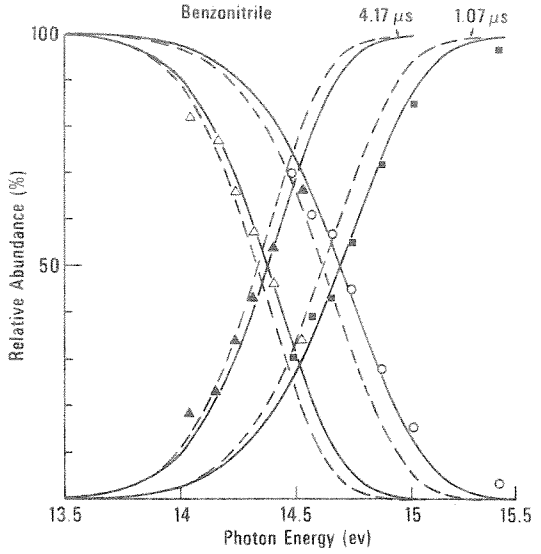

Fig. 3. — Comparison of calculated breakdown curves using the best fit parameters obtained here (—) with the parameters used by Chesnavich and Bowers (— —) (30). Experimental points: (△), (□), $C_6H_5CN^+$ parent; (▲), (■) $C_6H_4^+$ fragment.

normal mode frequency from 3100 cm^{-1} to 1500 cm and a second from 450 cm^{-1} to 150 cm^{-1}. Our results required only the lowering of one mode from 3100 cm^{-1} to 1500 cm^{-1}. As pointed out earlier (25), the choice of modes and their quantitative changes are without any deep significance. Other sets of frequencies can be found to fit as well.

The equivalent 1000 K entropies and Arrhenius preexponential A factors are much more meaningful and resemble the magnitude of the corresponding quantities found in thermal decompositions of neutral molecules when molecules are eliminated (33). Unfortunately there is no data on processes which are closely analogous. The very small equivalent activation entropy suggests on the one hand that the product $C_6H_4^+$ retains its ring structure and, on the other hand, that the transition state geometry is not dramatically different from that of the reactant ion. As a result the moment of inertia change will be small and little, if any, of the external rotational energy will be available for fragmentation (34, 35).

The kinetic parameters determined from the crossover sensitivity analysis specify a rate-energy dependence. This can be compared directly with an independent determination of this dependence done several years ago by Eland and Schulte (27). In their experiment they defined the photoexcitation energy by means of helium 58.4 nm radiation and selection of a particular narrow range of photoelectron energy. A mean rate constant was determined from an analysis of the time of flight distribution of ions decomposing in the accelerating field. Their results, along with the results of our own analysis are shown in Figure 4. It is seen that the rate energy dependence deduced from our analysis of time dependent breakdown curves is in very good agreement with those of Eland and Schulte. Also, our model for no contribution from external rotations is in significantly better agreement than the other. This is in pleasing contrast with our earlier comparisons with the results of Baer et al. on chlorobenzene and bromobenzene (36), where significant disagreement was noted. Also shown on the figure is the rate energy curve determined from the parameters used by Chesnavich and Bowers. These parameters were used in our calculations using the full Laplace transform method fro calculating sums and densities of vibrational states (37-39). The curve does not fit the experimental data nearly as well and, in fact does not agree with the rate-energy dependence that they computed (40) using the Whitten-Rabinovich method (41). There was a minor numerical error in their computations (42).

The activation energies, equivalent entropies and equivalent A factors are summarized in Table I, along with the activation energy which can be derived from the zero degree heat of formation for benzyme ion which was derived in a somewhat indirect manner from an earlier photoionization study of benzene (43). In that study is was noted that the experimental onset for the $C_6H_4^+$ ion was identical to that for $C_6H_5^+$ ion, and it was assumed that both had identical thresholds both of which were significantly displaced due to a large kinetic shift. This has now been directly verified, as was done earlier for the $C_4H_4^+$ ion from the same molecule by the more recent work of Eland et al. on pyridine (44). The resulting experimental heat of formation of benzyne ion is 1321 ± 10 J/mol. (316 kcal/mol.) at absolute zero, compared to our earlier estimate of ~ 1328 kJ/mol. (43). Assuming a vibrational heat capacity similar to benzene molecule we obtain a room temperature value of $\Delta H^\circ_{f_{298}}(C_6H_4^+) = 1311 \pm 10$ kJ/mol. (313 kcal/mol.). From the benzonitrile ionization potential, 9.70 eV, and the activation energy, 3.015 eV, we compute a fragmentation threshold of 12.72 ± 0.03 eV = 1227 ± 3 kJ/mol. slightly higher than the electron impact fragmentation threshold value 12.65 ± 0.1 eV obtained by Gordon and Reid (5) at long parent ion (~ 1200 μs) residence times. The lower electron impact threshold value is probably due to contribution of the internal thermal energy of the molecule, which amounts to about 0.1 eV on the average.

Grützmacher and Lohmann (45) measured an ionization potential for benzyne, 9.45 eV, and a linear isomer, 3-hexen-1, 5-diyne, 9.6 ± 0.2 eV using the RPD tech-

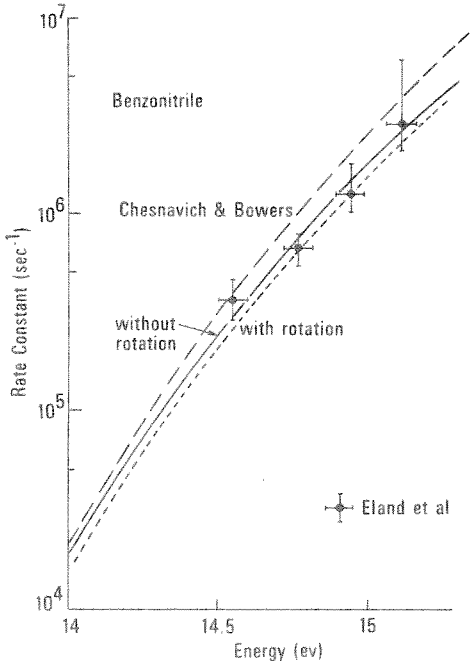

Fig. 4. — Calculated rate energy curves for bromobenzene. (—) present calculations with no rotation and with activated complex parameters which reproduce the data in Figure 1 (— — —) Same without rotation. (— —) present calculations with activated complex parameters used by Chesnavich and Bowers (30). (●) Experimental results of Eland and Schulte. (27).

nique. However, a more recent photoelectron spectroscopy study [46] gives 9.09 ± 0.02 for the average value of the cis and trans form of this linear isomer. Hence we take the benzyne ionization potential to be about 0.5 eV lower. We then obtain $\Delta H^{\circ}_{f_0}(C_6H_4) \approx 457$ kJ/mol. (109 kcal/mol.) and $\Delta H^{\circ}_{f_{298}}(C_6H_4) \approx 447$ kJ/mol. (107 kcal/mol.). The very good agreement between the $C_6H_4^+$ heat of formation derived here and inferred in the earlier benzene study strongly suggests that there is no significant reverse activation energy for both loss of HCN and loss of H_2 from the two respective parent ions.

It has been tacitly assumed that the ion and neutral structures of C_6H_4 represent the conventional benzyme, i.e. 1,2-dehydrobenzene. There are three neutral six carbon-ring isomers, each with a singlet and triplet state. A number of these have been invoked as reactive intermediates [47]. One has been trapped and the IR spectrum measured and analyzed to give convincing proof of its 1,2-dehydro structure [48]. Also a number of MO calculations have been carried out [49] which suggest that this structure may not necessarily be the most stable. The ionization potentials calculated by Dewar [49] would suggest that the 1,3-dehydrobenzene ion may be the most stable form, by about 1 eV. Thus it is not at all certain that the ion structure formed in the present work has the 1,2-dehydrobenzene structure. It is also possible to estimate with some confidence the neutral and ion thermochemical properties of three linear unstrained isomers using the neutral estimation scheme of Benson [50] and one ionization potential from photoelectron spectroscopy [46]. The results are shown in Table III, together with those obtained for the benzyne species analyzed in this study. It is clear that the species is not acyclic. It would be of interest to find experimental evidence for the formation of such an ion species at higher excitation energy.

TABLE III

Thermochemistry of Some C_6H_4 Neutral and Ion Species

Structure	$\Delta H^{\circ}_{f_{298}}$ neutral kJ/mol.	Ref.	IP eV	Ref.	$\Delta H^{\circ}_{f_{298}}$ Ion kJ/mol.
Benzyne	~447 ± 20	This work	~8.95	44,a	1311 ± 10
H-C≡C-C≡C-C(H)=CH$_2$	~534	est.[b]	(9.1)[c]	--	~1410
H-C≡C-C(H)=C(H)-C≡CH	~528	est.[b]	9.09 ± 0.02	46	~1403
H-C≡C, H-C≡C > C=CH$_2$	~506	est.[b]	(9.1)[c]	--	~1483

a. Corrected for a systematic error of about 0.5 eV see text.

b. Estimated using the Benson Procedure.[50]

c. Assumed approximately equal to the experimental value for 3-hexen-1,5-diyne.

Lastly, the kinetic parameters deduced from this analysis prove conclusively that the fragmentation process near threshold is preceded by internal conversion of electronically excited benzonitrile ions into vibrationally excited ions in the electronic ground state. In consequence, the conclusions of Cooks et al. [56] concerning the mechanism of kinetic energy release in fragmentation must be reexamined.

Summary and conclusion

The breakdown curve for the fragmentation show a strong dependence on residence time in the ion source. A detailed analysis of this effect leads to a rate energy dependence in very good agreement with an earlier study by Eland and Schulte. The kinetic parameters indicate that the fragmentation proceeds via a "tight" activated complex. in agreement with earlier conclusions of Chesnavich and Bowers, and that the fragmentation occurs from the parent ion electronic ground state. The activation energy for the process leads to a benzyne ion heat of formation very similar to that deduced from benzene photoionization, and it is shown that linear $C_6H_4^+$ isomers have a significantly higher heat of formation. Finally, the fragmentation threshold deduced here is quite close to that observed in electron impact at very long (1 200 μs) ion source residence times.

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